

# Lithium Superacid Salts For Secondary Lithium Batteries

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**Abstract:** Three newly prepared lithium superacid salts of the type  $C_nF_{2n+1}SO_3Li$  (where  $n$  is 4, 8, and 10) and  $CF_3SO_3Li$  and  $(CF_3SO_2)_2NLi$  were used as salts in polyethylene oxide (PEO) electrolytes. Our conductivity data show that among the salts investigated PEO electrolytes containing  $(CF_3SO_2)_2NLi$  gave the highest conductivity followed by  $C_4F_9SO_3Li$  and  $C_8F_{17}SO_3Li$ . PEO electrolytes containing  $C_{10}F_{21}SO_3Li$  and  $CF_3SO_3Li$  showed a lower conductivity at room temperature than the rest. Experimental Li-TiS<sub>2</sub> polymer cells containing either PEO- $C_4F_9SO_3Li$  or PEO- $(CF_3SO_2)_2Li$  as electrolyte were fabricated and tested for cycle life performance. No significant loss in capacity was observed even after 50 to 100 cycles.

Key words: lithium superacid salt, Polyethylene oxide, conductivity, cathode capacity and lithium transport number.

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## 1. Introduction

The ionic conductivity of polymer-salt complexes is affected by the salt used in the complex. For example, lithium salts with large anions such as  $CF_3SO_3$ ,  $(CF_3SO_2)_2$ ,  $BF_4$ ,  $ClO_4$ , etc. exhibit higher conductivity than salts with smaller anions like  $Br^-$  and  $Cl^-$ . The higher conductivity is, because of higher percentage of salt dissociation in the complex (due to low ion-ion interaction), and plasticizing effect of the anion (it mitigates or at least limits the phase changes of the polymer

by which the polymer becomes crystalline). Further, the plasticizing effect of the anion may reduce the glass transition temperature ( $T_g$ ) of the polymer which may in turn increase the ionic conductivity of the electrolyte. Indeed Armand et al [1] have synthesized lithium imide and studied as salt in PEO-based electrolytes. For example, PEO- $[(CF_3SO_2)_2N]Li$  exhibited a high conductivity of  $10^{-5}$  S/cm at room temperature in contrast to  $10^{-8}$  S/cm for traditional PEO-based electrolytes. Further, Lee Nest [2] prepared PEO-polyurethane based copolymer electrolytes containing the lithium imide salt which gave a room temperature conductivity of  $10^{-4}$  S/cm. We discuss below the results of our electrochemical study of electrolytes containing lithium superacid salts of general formula  $C_nF_{2n+1}SO_3Li$  (where n is 4, 8, and 10).

## 2. Experimental details

The new lithium superacid salts were prepared from the corresponding perfluoroalkane sulfonic acid ( $RF SO_3H$ ). The  $RF SO_3H$  was treated with excess aqueous lithium hydroxide (1.5 equivalent). The precipitated crude  $RF SO_3Li$  was dissolved in diethylether and excess  $LiOH$  was filtered. The ether layer was dried over anhydrous  $MgSO_4$ , filtered and ether evaporated to obtain pure  $RF SO_3Li$ . The lithium salt was dried at  $100^\circ C$  in air and used without further purification. Polymer electrolytes were prepared as follows. Lithium superacid salt was dissolved in about 100 ml of methanol followed by the addition of appropriate amount PEO. Oxygen to lithium ratio in the electrolyte was 8:1, the solution was stirred and heated slowly to  $50^\circ C$  to dissolve the PEO completely and the solution was poured into a Teflon mold. The solution was allowed to evaporate at room temperature. The dried film was pumped in vacuum for 48 hrs at  $10^{-5}$  Torr. This procedure yielded films of thickness around  $75 \mu m$ . The films were cut to size for electrochemical evaluation. Since free standing electrolyte films containing  $(CF_3SO_2)_2N Li$  could not be prepared easily, they were cast either on stainless foil for film studies or on electrodes (composite cathode) for cell studies. Composite cathodes containing PEO, lithium salt and  $TiS_2$  of about 40 mAh capacity were prepared for cell studies in conjunction with metallic lithium as anode. In the composite cathode the ratio of oxygen to lithium is 8:1: same as in the electrolyte.

Standard electrochemical equipment were used for a-c and d-c measurements and are described elsewhere [3].

### 3. Results and Discussion

The electrolytes were evaluated for their bulk conductivity, lithium transport number and voltage window. The films were cut to size for electrochemical evaluations.

#### 3.1. Bulk Conductivity

The bulk conductivity of the films sandwiched between two Li foils was evaluated as a function of temperature by a-c impedance technique. In **Figure 1** are given the bulk conductivity, obtained from a-c measurement, as a function of reciprocal temperature for all the PI:O-based electrolytes containing lithium superacid salts. In **Table 1** are given the conductivity values, culled from **Figure 1** at pre-selected temperatures, for the different electrolytes. The data in the above table indicate that the:

- 1) PI:O-based electrolytes containing C<sub>4</sub> and C<sub>8</sub> salts exhibit higher room temperature conductivity  $\gamma$  compared to that containing CF<sub>3</sub>SO<sub>3</sub>Li.
- 2) PI:O-based electrolytes containing C<sub>10</sub> salt exhibited lower conductivity compared to the PI:O electrolytes containing C<sub>4</sub> and C<sub>8</sub> lithium superacid salts. This observation suggests that the conductivity may go through a maximum between CF<sub>3</sub>SO<sub>3</sub>Li and C<sub>10</sub>F<sub>21</sub>SO<sub>3</sub>Li.
- 3) lithium ion conductivity  $\gamma$  of PI:O-based electrolyte containing (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NLi is the highest among the electrolytes investigated.

#### 3.2.1 Transport Number

Several electrochemical and non-electrochemical techniques have been used to determine the transport number of ions<sup>4</sup> in polymer electrolytes. In this study we have employed a combination of a-c and d-c techniques to determine the lithium transport number in the electrolytes. Cation transport number ( $t^+$ ) is related to the bulk resistance ( $R_b$ ) and diffusional impedance ( $Z_d$ ) by the following equation.

$$t^+ = R_b / (R_b + Z_d)$$

where  $R_b$  the bulk resistance was determined from a-c measurements as described earlier and  $Z_d$  the diffusional impedance was determined from d-c measurement as described elsewhere<sup>4</sup>. In **Table-1** the values of transport number for  $Li^+$  in PEO-based electrolytes are given along with the conductivities at around 80°C. The  $t^+$  for  $Li$  ions is around 0.3 which is similar to what has been reported in the literature for similar systems [5].

**Table 1. Electrolyte Properties**

| Electrolytes   | Conductivity (S/cm)  |                     |                     | Transport number<br>(~80°C) |
|--|----------------------|---------------------|---------------------|-----------------------------|
|  | RT                   | ~60°C               | ~80°C               |                             |
| PEO/C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> Li     | 10 <sup>-6</sup>     | 10 <sup>-4</sup>    | 5x 10 <sup>-4</sup> | 0.3 -0.4                    |
| PEO/C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> Li    | <10 <sup>-6</sup>    | 5X 10 <sup>-5</sup> | 10 <sup>-4</sup>    | 0.3 -0.4                    |
| PEO/C <sub>10</sub> F <sub>21</sub> SO <sub>3</sub> Li   | 10 <sup>-6</sup>     | 7X 10 <sup>-6</sup> | 5x 10 <sup>-5</sup> | 0.3 -0.4                    |
| PEO/CF <sub>3</sub> SO <sub>3</sub> Li                   | 7 x 10 <sup>-8</sup> | 10 <sup>-5</sup>    | 5X 10 <sup>-5</sup> | 0.3 -0.4                    |
| PEO/(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NiLi | 7x 10 <sup>-5</sup>  | 4X 10 <sup>-3</sup> | 7x 10 <sup>-3</sup> | 0.3 -0.4                    |

### 3.3. Voltage Window

in order to assess the usefulness of these electrolytes for use in conjunction with high voltage cathodes such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> etc. the effective voltage window was determined. A 1cm<sup>2</sup> area electrolyte was sandwiched between two flat well polished Ni or stainless Steel (SS) electrodes (blocking contacts) and the voltage was scanned slowly at 1 mv/sec. No appreciable Faradaic or break-down current was observed for the electrolytes in the potential regime 1.4 to 4.5 V. The data seem to suggest that all these electrolytes could potentially be used in conjunction with high voltage cathodes.

### 3.5. Fabrication and Testing of Cells

Experimental cells with Li anode and TiS<sub>2</sub> cathode were fabricated for cycle life performance evaluation. The two electrolytes selected for evaluation in full cells are PEO/C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>Li and PEO/(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>NiLi. Pancake-type flat prismatic cell design was selected for the fabrication of

experimental cells. The electrolyte film was sandwiched between Li anode and  $\text{TiS}_2$  composite cathode and the entire electrode stack was housed in a polyethylene laminated aluminum foil bag. The cell is case neutral in design.

### 3.6. Composite Cathode

Composite cathode consists of a cathode material, a polymer electrolyte, usually same as the electrolyte, and an electronic conductor like carbon. To achieve higher rates and cycle life composite cathodes should possess good ionic and electronic conductivity. While the electronic conductivity is associated with the cathode itself, the ionic conductivity is due to both the electrolyte and the cathode material. Since  $\text{TiS}_2$  is a good electronic conductor no conducting diluents were added to the composite. Polymer electrolyte containing PEO and either  $\text{C}_4\text{F}_9\text{SO}_3\text{Li}$  or  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$  was added to the composite as binder. Composite cathode was prepared by a solution casting technique as in the case of polymer electrolyte, described previously. Exact amount of lithium salt was dissolved in methanol followed by the addition of PEO weighed before hand. The solution was heated to  $50^\circ\text{C}$  with stirring to dissolve the PEO. To the homogeneous solution was added appropriate amount of  $\text{TiS}_2$  and the solution was stirred well to disperse  $\text{TiS}_2$  particles uniformly in the solution. The solution was poured onto a stainless steel foil (precleaned) kept at the bottom of a Teflon mold. The solution was allowed to evaporate slowly. After complete evaporation of the solvent, the film was pumped in vacuum at  $40-50^\circ\text{C}$  for two days. This procedure yielded thin films of thickness  $\sim 100\text{ }\mu\text{m}$ . Several volume ratios of  $\text{TiS}_2/\text{PEO}$  ranging from 20/80 - 80/20 were investigated. Exact amount of lithium salt was added to the composite cathode to yield O:Li ratio of 8:1. Among the several compositions investigated the one with 1:1 volume ratio of  $\text{TiS}_2/\text{PEO}$  was selected for further investigation since the cathode films gave good cycle life and could be handled easily.

### 3.7. Cell Testing

The cells were heated to  $60^\circ\text{C}$  for cycle life performance studies at 100% depth of discharge (DOD). The cells were charged and discharged by constant current method. The cells were cycled between 1.7 and 2.7 volts. In Figures 2, 3 & 4 the capacity of the cells at different

discharge rates are given, All the cells showed roughly 33% of the initial capacity. However, they could be cycled over 50 cycles with out significant loss in capacity, The cells containing imide salts (due to higher conductivity, Table 1.) could be discharged at higher rates over cells containing  $C_4F_9SO_3Li$ . However, one area which needs further improvement and optimization is cathode utilization. Optimization of the composition and loading of the composite cathode are in progress.

#### 4. Conclusions

Several PEO-based true polymer electrolytes containing lithium superacid salts were prepared and studied for their electrochemical properties. PEO electrolytes containing  $C_4F_9SO_3Li$  and  $C_8F_{17}SO_3Li$  exhibited higher room temperature conductivity compared to that containing  $CF_3SO_3Li$  (lithium triflate) and  $ClO_4Li$ . This observation suggests that the bulk conductivity may go through a maximum between  $CF_3SO_3Li$  and  $ClO_4Li$ . Electrolyte films containing lithium imide salt exhibited higher conductivity among the electrolytes investigated. Experimental Li-TiS<sub>2</sub> polymer cells were fabricated and tested for cycle life performance. The electrolytes evaluated at the cell level were PEO- $C_4F_9SO_3Li$  and PEO- $(CF_3SO_2)_2NLi$ . No significant loss in capacity was observed even after 50-100 cycles.

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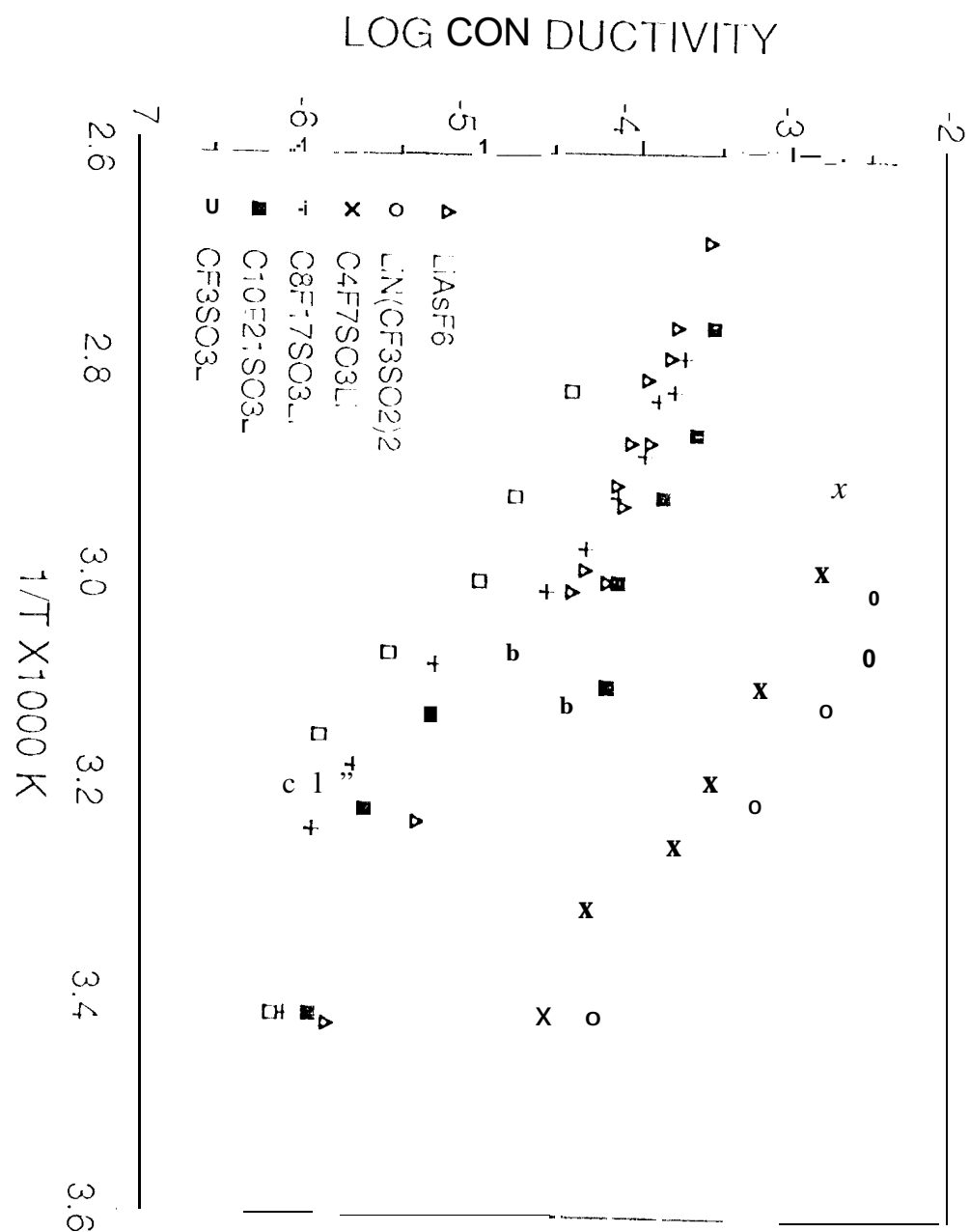
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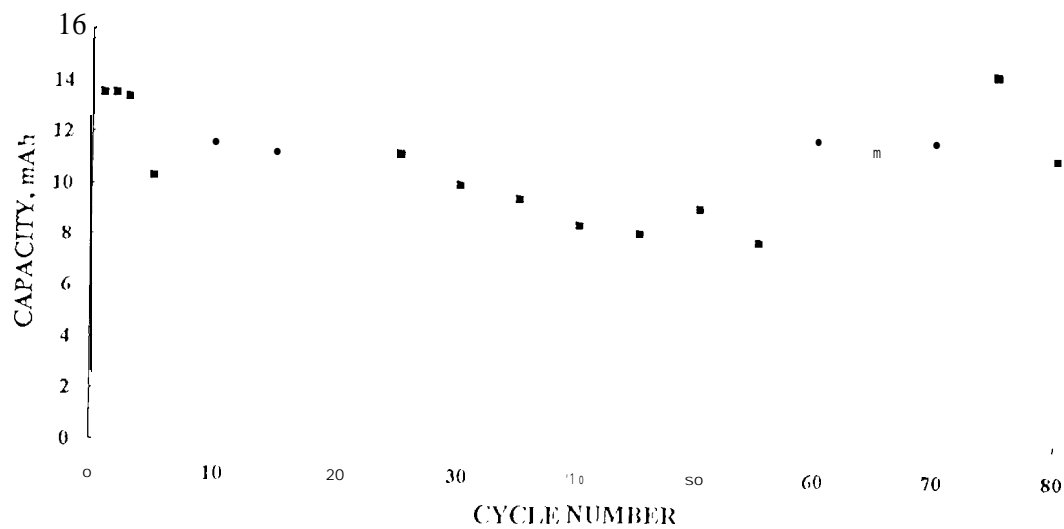
## Figures

- Figure 1. Plot of conductivity  $\kappa$  vs.  $1/l$  for PEO-based electrolytes containing lithium superacid salts
- Figure 2. Capacity vs. cycle number for  $\text{Li/PEO}-(\text{CF}_3\text{SO}_2)_2\text{NLi/TiS}_2^*$ . Cell at  $60^\circ\text{C}$ . The discharge currents were 5 mA and 3 mA before and after 55 cycles, respectively. The charge current was 1 mA. \*: composite cathode.
- Figure 3. Capacity vs. cycle number for  $\text{Li/PEO}-(\text{CF}_3\text{SO}_2)_2\text{NLi/TiS}_2^*$ . Cell at  $60^\circ\text{C}$ . The discharge and charge currents were 4 mA and 1 mA respectively. \*: composite cathode.
- Figure 4. Capacity vs. cycle number for  $\text{Li/PEO-C}_4\text{F}_9\text{SO}_3\text{Li/TiS}_2^*$ . Cell at  $60^\circ\text{C}$ . The discharge currents were 0.5 mA and 1 mA before and after 2 cycles, respectively. The charge current was 0.5 mA. \*: composite cathode.

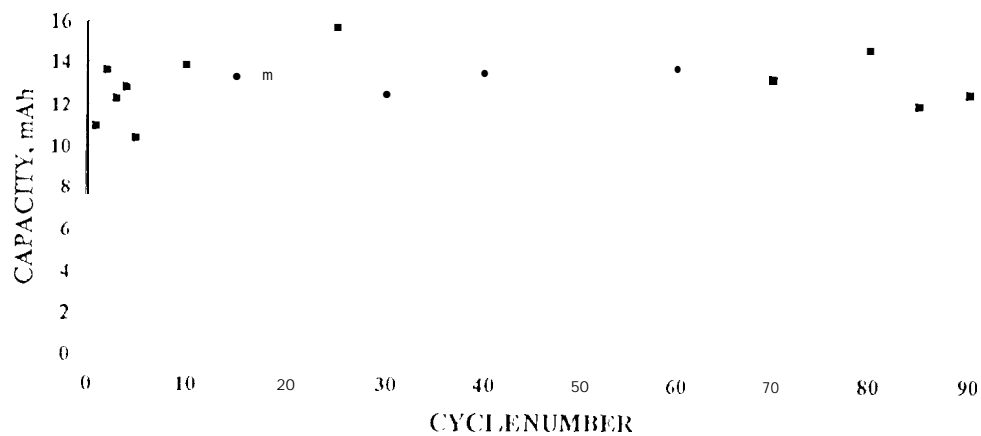




CYCLE LIFE OF Li-TiS<sub>2</sub> CELL WITH IMIDE/PEO @ 60 C



CYCLE LIFE OF Li-TiS<sub>2</sub> CELL WITH IMIDE/PEO @ 60 C



CYCLE LIFE OF Li-TiS<sub>2</sub> CELL WITH C<sub>4</sub> SALT/PEO @ 60 C

